Spectroscopic observations of nanosized TiO_2 by the hydrothermal method

Mohamed Zikriya, Y. F. Nadaf, P. Vijai Bharathy, and C. G. Renuka

Citation: AIP Conference Proceedings **1953**, 030228 (2018); doi: 10.1063/1.5032563

View online: https://doi.org/10.1063/1.5032563

View Table of Contents: http://aip.scitation.org/toc/apc/1953/1

Published by the American Institute of Physics

Spectroscopic Observations of Nanosized TiO_2 by the Hydrothermal Method

Mohamed Zikriya[1], Y F Nadaf[2], P. Vijai Bharathy[3] and C G Renuka[1*]

[1]*Department of Physics, Bangalore University, Bengaluru-560056 India*
[2]*Department of Physics and Research Center, Maharani's Science College for Women Bengaluru-560001. India*
[3]*Department of Physics, CBM college, Kovaipudur, Coimbatore – 641 042.India*

[*]Corresponding author: renubub@gmail.com

Abstract. Metal oxides are useful materials that have various applications in advanced field such as, in view of their different properties, hardness, thermal dependability and compound resistance. Novel utilizations of the nanostructures of these oxides are drawing in critical enthusiasm as new preparation process are created and new structures are described. Hydrothermal synthesis is a fruitful procedure to prepare different sensitive structures of metal oxides on the scales from a couple to several nanometres, particularly, the hugely scattered middle structures which are hardly through pyro-preparation.Titanium dioxide nanocrystals are synthesis by a hydrolysis procedure of metatitanic acid. Nano precious crystal of different sizes is procure in the after calcinations from 150 to 225°C. Raman scattering was utilized to examine the advancement of the anatase stage in the nano crystal during calcinations.

INTRODUCTION

Oxides frame one of the larger functions of inorganic alloys both in nature and in the research centre. The hydrothermal process is a standout amongst the most well known methods for developing these high-temperature oxides, multiple oxides and low-temperature changes of the oxides [1]. The work on the hydrothermal process amalgamation of oxides started amid the 19th century with quartz in 1845 followed by this, substantial scale explore research started amid the 1890s, on allotrope and other relevant high temperature oxides. Today, discovery abundant gotten by the hydrothermal synthesis: Fe_2O_3, HfO_2, ZrO_2, Cu_2O, Bi_2O_3, BeO, Al_2O_3, In_2O_3, TiO_2, ZnO, to specify a couple, and an vast assortment of different oxides. Some of these convey extraordinary essentialness as fabricated and some as component materials [2].

In this way, the hydrothermal procedure gives particular favourable circumstances to a preparative scientific expert to get an extensive assortment of hydroxides, hydroxyl carbonates, hydroxylchlorides, and so on, of different metals [3].The procedure includes the absorption of a photon by TiO_2, prompting the advancement of an electron from the valence band to the conduction band and consequently creates an electron hole. The electron in the conduction band is then expelled by responding with O_2 in the external system. The hole in the valence band can respond with OH-or H_2O variety, which are immersed on the surface of the TiO_2 to give the hydroxyl profound [4]. This hydroxyl radical starts the photocatalytic decomposition, a contamination regulate innovation or diversification technology which obliterates the natural synthetic impurity in air, water, and soil. It may be utilized to hold the dirtied water both ground water and surface, correspondingly spoil the drinking water and soil. The system can be utilized as a modern contamination manages method for purification upvaporous and fluid spoil streams consists of organic composite. The photocatalytic movement of TiO_2 relies on its crystal arrangement of rutile, or anatase, surface field, porosity, size dispersion, and of dopant existence, surface hydroxyl density, and so on. These elements impact specifically on the generation of electron-hole pairs, the surface desorption and adsorption prepare and the redox procedure. There are a few methods for synthesis TiO_2 particles. The hydrothermal method has many profits like delivering an exceedingly homogeneous crystalline product, which can be acquired straightforwardly at moderately bring down response temperature[3,5].

2nd International Conference on Condensed Matter and Applied Physics (ICC 2017)
AIP Conf. Proc. 1953, 030228-1–030228-5; https://doi.org/10.1063/1.5032563
Published by AIP Publishing. 978-0-7354-1648-2/$30.00

MATERIALS AND METHODS

In this work, Ilmenite extract where reduced to metatitanic acid using from sulphate process. Metatitanic acid was used as a source material for the preparation of Titanium dioxide. The detailed methodology for the preparation of metatitanic acid is reported in Mohan Das et al [6], concentrated H_2SO_4, and ammonia (NH_3) were all of analytical grade purchased from Sigma Aldrich, having 96 % of purity used. Deionised water was obtained from laboratory purification system. The combination of TiO_2 is generally done in little autoclaves, furnished with Teflon liners. The conditions chosen for the synthesis of TiO_2 particles are: T = >150°C, P < 100 bars. Such pressure temperature conditions encourage the utilization of autoclaves of straightforward outline given Teflon liners. The utilization of Teflon liners has gotten unadulterated and homogeneous TiO_2 particles.

In this study, the precursor was a mixture of 6.5g Metatitanic acid dissolved in 4ml of concentrated sulphuric acid (H_2SO_4) and heats the mixture at 70 ^oC for 30 minutes, a clear solution formed. The solution is neutralized by adding ammonia (NH_3OH) solution till the pH of the solution is 7. The chemical reaction was start when solutions are mixed together under vigorous stirring in the magnetic stirrer for 1hour at 400 RPM. Hydrolysis of Metatitanic acid gives a turbid solution which heated up to 65 –70 ^oC for about 1hour (peptization). After peptization, the volume of the solution decreases, In the hydrothermal method, precipitates was transfer to a stainless steel Teflon lined autoclave, kept the autoclave in a muffel furnace at temperature ranging from 150 ^oC to 225 ^oC for 24 hours, and aged at room temperature for 4hours. The hydrothermally treated precipitate was then centrifuged; the precipitate was recollected by treated with deionized water and ethanol, after washed with ethanol and dried at 45^oC for 20 minutes, a white - yellow powder was obtained. Finally, the obtained powder was grained and annealed at a temperature 80 ^oC 12 hours. The obtained sample were characterize by the crystalline phase of the nanoparticles analyzed with the aid of X-Ray Diffraction (XRD) use of a Rigaku diffractometer with Cu target K_α radiation (λ=1.54Å), and Raman studies of the samples (powder) have been received by Ventana Raman spectrometer with CCD. For the emission 785 nm diode laser was used as the excitation source.

RESULT AND DISCUSSIONS

Powder X-Ray Diffraction (XRD)

The crystallographic data of all samples was characterized by powder X-ray diffraction. The specimens were set up as fine homogeneous powder. The diffracted X-ray compare to all arrangements of planes in the crystal powder which could be orientated in each available course in respect to the X-ray bar. The XRD pattern intensity versus 2 theta (2θ) were recorded, commonly from 10° to 80° at a scanning speed of 2° for each minutes.

In order to study the structural properties of the prepared TiO_2 sample, the XRD is an powerful technique to help in analyze the crystal phase and size of the nanocrystallities, it was found that the sample structure is sensitive to the annealing temperature. From figure 1, the XRD pattern of TiO_2 sample annealed at different temperatures, namely 150^oC, 175 ^oC, 200 ^oC and 225 ^oC at 24hr. In XRD pattern there are five peaks were observed at 25.29^o, 37.88^o, 48.02^o, 53.99^o and 62.73^o in the 2theta range, the pattern for pure TiO_2 are identified and associate to the diffraction faces of the (101), (004), (200), (105) and (204) planes respectively, diffraction peaks is used to determine the average crystallite size employing the Debye-Scherrer's formula[7] (Equation 1) and it was found to be around 14nm.

$$d = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

These results show that the standard JCPDS card no. 21-1272 belongs to the tetragonal anatase TiO_2 phase with space group $I4_1/amd(141)$ also establish the development of single phase polycrystalline in nature. Crystallite size and strain are determined by using Williamson-Hall[8] equation (2).

$$\beta \, \mathrm{Cos}\,\theta = \mathrm{k}\lambda/\mathrm{D} + 4\varepsilon \sin\theta \tag{2}$$

Where 'β' is observed full width half maxima, 'θ' is the Bragg's angle, 'k' is the Scherer's constant, 'λ' is the wavelength X-ray used, 'D' is the crystallite size and'ε' is the strain in the crystal. Table 1 shows the average crystallite size for pure TiO2 found to be in range between 8-14 nm, and no other phases are detected nor displacement of 2 θ angle. In annealed samples, there is an obvious diffraction peak at 25.29o which corresponds to the (101) crystalline plane of the TiO2 anatase phase at 25.35o 9, such preferred orientation as also observed for TiO2 sample at different annealing temperature for 2hours. The shifts of diffraction peaks for annealed sample to greater scattering angles will

advice a stress satisfaction in the sample. It is basic to note that while extensive height with low forces may be a result of amorphism, they may in likewise be a direct result of small crystallite sizes peak extending. Stacking Fault probability while the cause gives data about the microstrain of the lattice section.

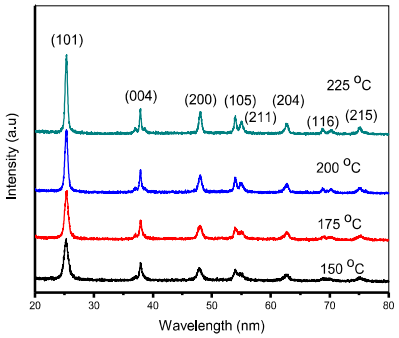

FIGURE 1. XRD pattern of the synthesis of pure TiO_2 by Hydrothermal method.

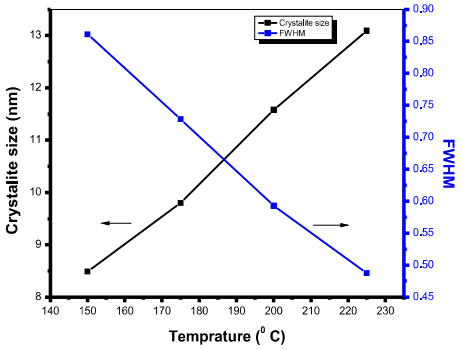

FIGURE 2. Variation of FWHM and grain size of pure TiO_2 nano particle with different temperature.

This implies the geometry of the crystallites is not spherical shape. The microstrain parameter of the lattice can probable is related with the viable crystallite size in the accompanying way: the estimation of the adequate crystallite size increments when the microstrain esteems reduction.

Figure 2 shows the variation of FWHM and crystallite size of TiO_2 nanoparticles with calcinations temperature for the samples prepared at 150-225 ºC for 24 hours. It has a linear variation with the calcinations temperature. The grain size increases from 8 nm to 14 nm as the increase the calcinations temperature of the sample.

TABLE 1. Structural parameters obtained from XRD patterns of pure TiO2with different temperature.

Calcinations temperature	Beta (β)	2θ (degree)	FWHM	Dislocation density	Stacking Fault	Strain	Crystal Size (nm)
150 0C	0.0157	25.27	0.8610	36.88	0.4603	0.05376	8.49
175 0C	0.0123	25.29	0.7283	36.95	0.3886	0.003686	9.80
200 0C	0.0108	25.23	0.5927	36.96	0.3161	0.000645	11.58
225 0C	0.0102	25.26	0.8745	36.92	0.2603	0.001376	13.09

Here it is proper to specify the titania particle size is a basic component for the execution of the material in the photocatalytic movement, and the monodispersed nanoparticles are the best reason ones. It has been demonstrated that the molecule size is an essential consider the elements of the electron - hole recombination handle, which balances the advantages from the ultrahigh surface range of nanocrystalline TiO2. The prevailing electron-hole recombination procedure might be distinctive for TiO2.

Raman Spectra

Synchronous cross peaks show the bands at 633, 511, and 393 cm^{-1} (Figure 3), while the synchronous cross peaks demonstrate those at 641, 517, and 398 cm^{-1}. Groups identified in 2D relationship spectra emphatically uphole that all groups move into a greater intensity with increasing the particle diameter. All the bands in Raman spectra band move to greater intensity can be clarified by the impact of variation in particle size on the constrain constants. At the point when the molecule size decline to the nanometer scale, a volume narrowing happens inside the nanoparticles and starts increments in the drive constants therefore of the increases in the interatomic separations. Subsequently, the Raman force move towards a higher intensity because of the expanding force constants. In this review, accordingly, the band move of TiO_2 nanoparticles recommend that size-incited radial pressure in TiO_2 nanoparticles and these outcomes in a volume constriction. Likewise, the synchronous relationship range has all positive cross peaks at 633, 511, and 393cm^{-1}, which uncovers that force of these groups increasing simultaneously with increasing the particle size. Conversely, Xu et al. have attempted to clarify the variety in the Raman band with a phonon confinement[10]. On the basis of the Heisenberg uncertainty principle. The particle size increases, the phonon is progressively confined within the particle and the phonon movement increases. This widening of the phonon movement prompts the scattered phonon force as indicated by the law of conservation of energy. The Raman spectra of an anatase single crystal has

been examined by Ohsaka[11], who inferred that the modes show up at 399 cm^{-1} (B_{1g}), 513 cm^{-1} (A_{1g}), and 639 cm^{-1} (E_g).

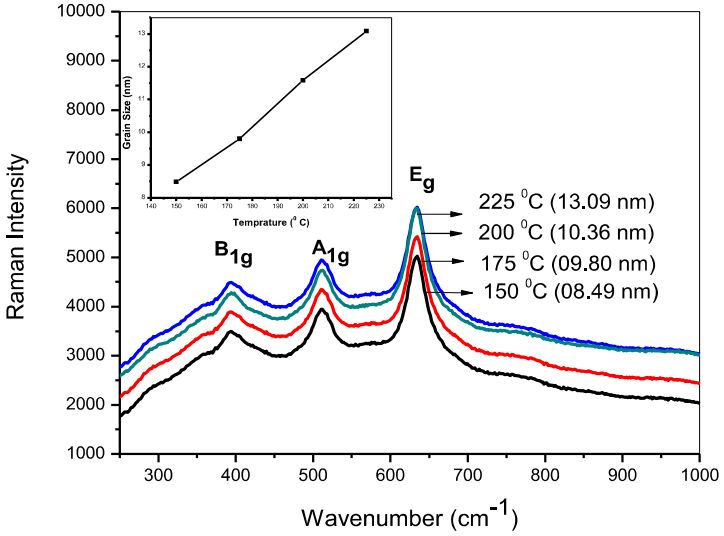

FIGURE 3. Raman spectra of the synthesis of pure TiO2 by Hydrothermal method

TABLE 2. Wavenumber and FWHM (in parentheses) Raman Spectra of pure TiO_2

Calcinations Temperature	B_{1g} (cm^{-1})	A_{1g} (cm^{-1})	E_g (cm^{-1})
150 0C	393.4 (24.26)	511.1 (25.44)	633.3 (25.97)
175 0C	392.6 (27.92)	511.1 (25.44)	634.0 (26.13)
200 0C	393.4 (35.32)	510.4 (25.93)	633.3 (26.32)
225 0C	394.1 (24.96)	511.1 (23.62)	633.3 (25.99)

In this review, we doled out and translated the Raman groups of the TiO_2 nanoparticles utilizing prior outcomes acquired for the mass phase. Fig. 3 demonstrates the Raman spectra of the all samples of TiO_2 nanoparticles. The differences between the spectra all the more precisely, the wavenumbers and the Full-Widths at Half- Maxima (FWHM) of the Raman bands are depicted in Table 2. The primary components of the spectra of all samples with different temperature are fundamentally the same as those of the evidence TiO_2[10, 12], which implies that the anatase phases of the nanoparticles of all samples have a specific level of long-range form; obviously the Raman band shift towards higher intensity generally increases as the particle size increases

CONCLUSIONS

TiO_2 nanoparticles were prepared by hydrothermal technique. The impact of concentration of the precursors, temperature and time of development on the structure, grain size, were analyzed. The XRD analysis exhibits that the nanoparticles have the tetragonal structure and the particle size 8 nm – 14nm increments with increasing with temperature. In this work, we reported spectroscopy in characterization of Raman spectra of different range size TiO_2 nanoparticles. The Raman examination precisely demonstrated that all Raman bands shift into a greater intensity with increasing particle size of TiO_2 nanoparticles. The source of Raman bands shift can be ascribed to the impact of littler particle size and it influences the force constant.TiO_2 particles with a excessive level of crystalline and the coveted size and shape could be accomplished through a methodical comprehension of the hydrothermal. Distinctive particle size measure administrations have been set up for enhancing the photocatalytic efficiencies of various systems.

ACKNOWLEDGEMENT

The authors are grateful to the DST (SERB) New Delhi for providing financial support through major project No.SR/S2/CMP/-0069/2012. Thanks to Prof. Sharath Ananthamurthy, Coordinator DST-PURSE Programme for Raman characterization Bangalore University, Bengaluru. Thanks to Director, Directorate of Minorities, Government of Karnataka.

REFERENCES

1. M. Rajabi, S. Shogh and A. Iraji Zad, J. Lumin. 157, 235-242 (2015).
2. D.A.H. Hanaor and C.C. Sorrell, J. Mater. Sci. 46, 855-874 (2011).
3. M. Wei, Y. Konishi and H. Arakawa, J. Mater. Sci. 42, 529-533 (2007).
4. M. Vijay, P. V. Ananthapadmanabhan and K.P. Sreekumar, Appl. Surf. Sci. 255, 9316-9322 (2009).
5. K.B. Jaimy, S. Ghosh and K. Gopakumar Warrier, J. Solid State Chem. 196, 465-470 (2012).
6. V. Ahmed Yasir, P.N. Mohan Das and K.K.M. Yusuff, Int. J. Inorg. Mater. 3, 593-596 (2001).
7. A.Teherniya and D. Raoufi, Semicond. Sci. Technol. 31, 125012-9 (2016).
8. V. Mote, Y. Purushotham and B. Dole, J. Theor. Appl. Phys. 6, 6 (2012).
9. V.S. Smitha, S. Pillai, U.N. Saraswathy Hareesh and K.G. Warrier, RSC Adv. 4, 61727-61735 (2014).
10. W.S. Li, Z.X. Shen, H.Y. Li, D.Z. Shen and X.W. Fan, J. Raman Spectrosc. 32, 862-865 (2001).
11. Tohiaki Ohsaka, J. Phy. Soc.of Japan. 48, 1661-1668 (1980).
12. H.C. Choi, Y.M. Jung and S. Bin Kim, Vib. Spectrosc. 37, 33-38 (2005).